3 Analysis of Variations in Particulate Matter

3.1 Day-of-Week Patterns of Particulate Matter and its Species at Selected Sites in California

3.1.1 Abstract

This chapter summarizes an analysis of variations, by day of week, in concentrations of particulate matter (PM) in California. Because volatile organic compounds (VOCs) and oxides of nitrogen (NO_X) are not only precursors of ozone but also of secondary PM, it is useful to know whether the variations by day of week in these precursors are also evident in PM data. Concentrations of PM ≤ 10 microns and ≤ 2.5 microns in aerodynamic diameter (PM10, PM2.5) were analyzed. Analysis of PM concentrations indicates a general weekly pattern with the maximum occurring late in the workweek and the minimum occurring on weekends (especially Sunday); however, this pattern does not prevail at all sites and areas.

Given the wide variety of sources contributing to primary and secondary PM and the factors listed above, interpretation of these results in terms of weekday/weekend emissions differences is complex and should be done with caution. More hourly PM data and a more comprehensive air quality data analysis, as well as a three-dimensional modeling study testing the impact of changes in emission levels, timing, spatial distributions, etc., would lead to a more accurate characterization of the weekday/weekend pattern of PM and the major contributing factors.

3.1.2 Introduction

Airborne PM is not a single pollutant, but rather a mixture of primary and secondary aerosols containing many subclasses of pollutants with each subclass potentially containing many different chemical species. In California, the proximity of a location to a variety of sources, in addition to the diurnal and seasonal variations in meteorological conditions, causes the size, composition, and concentration of particulate matter to vary in space and time. Although PM pollution still remains the most serious and complex air pollution problem facing both scientific communities and regulatory agencies, exceedances of PM standards have become less frequent (Table 3.1-1). Despite large increases in population and the number of vehicle miles traveled, California has been able to achieve both significantly cleaner air and major economic growth.

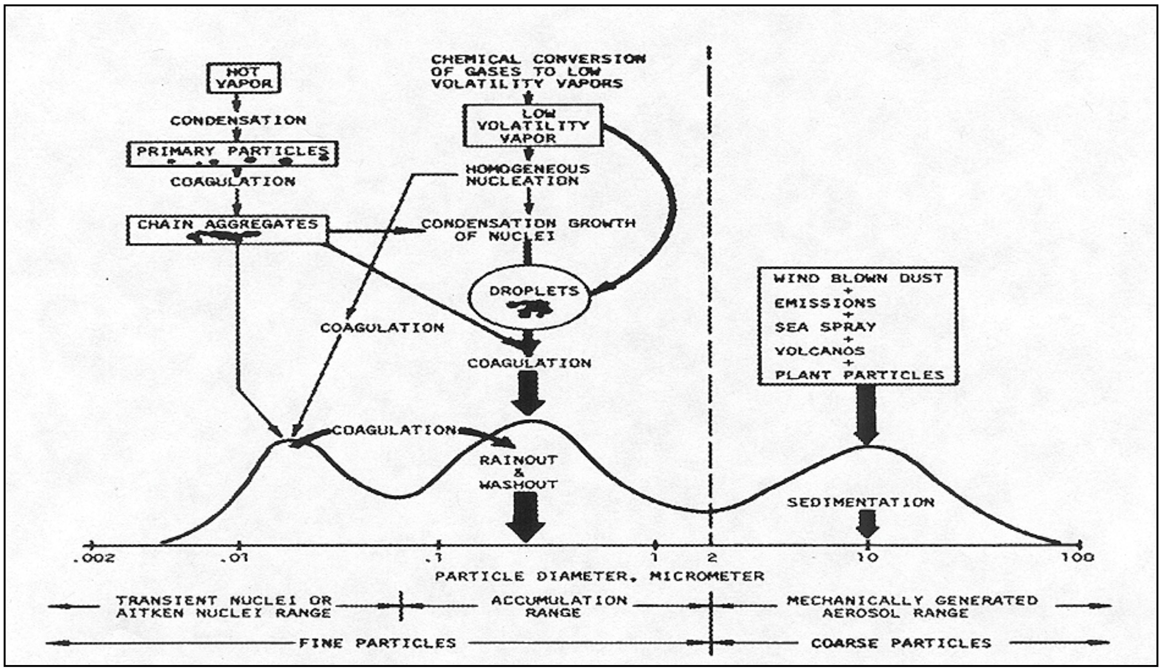
Particulate matter can exist in the liquid or solid phase and its size can span several orders of magnitude, from a molecular cluster of 0.005 µm in aerodynamic diameter to coarse particles on the order of 100 µm. Figure 3.1-1 shows the idealized atmospheric aerosol size distribution, featuring three different aerosol groups (Whitby and Cantrell, 1976). The figure shows the mechanisms such as condensation and coagulation that transfer aerosol mass from one size range to another. The number distribution is dominated by particles smaller than 0.1 μm, while most of the surface area is in the 0.1 to 0.5 size range. On the contrary, the aerosol mass distribution has usually two distinct modes, one in the submicron regime (referred to as accumulation mode) and the other in the coarse particle regime.

The literature includes references to fine, coarse, suspended, respirable, inhalable, thoracic and other objectives to indicate a size segregation of particulate matter (PM). Uniform criteria are not always employed in the application of these designations. Particles less than 2.5 μm in aerodynamic diameters are generally referred to as "fine" and those greater than 2.5 μm diameters as "coarse". The selection of PM10 as an indicator was based on health considerations and was intended to focus regulatory concern on those particles small enough to enter the thoracic region.

In addition to falling into different size ranges, fine and coarse particles differ in formation mechanisms, chemical composition, sources, and exposure relationships. Fine PM is derived from combustion material that has volatilized and then condensed to form primary PM and from precursor gases (such as sulfur dioxide, nitrogen oxides, and certain organic compounds) reacting in the atmosphere to form secondary PM. Coarse PM, in contrast, is formed by crushing, grinding, and abrasion of surfaces, which breaks large pieces of materials into smaller pieces. These particles are then suspended by wind or by anthropogenic activity such as construction, mining, and agricultural activities. As the particles respond to their variations in their atmospheric environment, their chemical and physical properties - and hence their characteristics, such as light scattering and toxicity - can change by accumulation of atmospheric gas-phase chemical reaction products or through heterogeneous reactions with gas-phase species.

The health effects of particulate matter vary depending upon the size of the particles. While both fine and coarse particulate matter can accumulate in the respiratory system and aggravate problems such as asthma, fine particles are more likely to embed deep within lung tissue and, more so than coarse particles, contribute to other detrimental health effects. According to recent community epidemiological studies, adverse health effects associated with both short-term and long-term exposure to fine particles include increased premature deaths, primarily in the elderly and those with heart or lung disease; aggravation of respiratory and cardiovascular illness, leading to increased hospital visits; lung function problems and symptoms similar to chronic bronchitis, especially in children and asthmatics; increased work and school absences; and alterations in lung tissue structure and in respiratory tract defense mechanisms (CARB/OEHHA, 2000; Gauderman et al., 2002).

Figure 3.1-1. Idealization of an atmospheric surface area distribution showing the principal modes, sources of mass, and the processes involved in mass transfer and removal (Whitby and Cantrell, 1976).



Gaseous sulfur dioxide emitted from fossil fuel combustion, as well as organic species emitted from both anthropogenic and biogenic sources, can react in the atmosphere to form particulate sulfates or secondary organic aerosols, respectively. In fresh NO_X emissions, which primarily consist of nitric oxide (NO) and smaller amounts of nitrogen dioxide (NO_2), the NO undergoes reactions with ozone and peroxy radicals to form additional NO_2. The NO_2 can be directly converted to nitric acid (HNO_3) via a homogenous gas-phase reaction with the hydroxyl radical. This is the principle formation mechanism for nitric acid in the daytime (Finlayson-Pitts and Pitts, 2000). HNO_3 is also formed at night via the hydrolysis of the NO_3 and N_2O_5 on surfaces. The major chemical loss process for gas-phase nitric acid is its reaction with gaseous ammonia to form ammonium nitrate (NH_4NO_3). This reaction, which is reversible, is believed to be the major source of fine (<2.5 μm diameter) nitrate aerosol in California's urban air. Deposition to surfaces is also a major loss process of HNO_3.

The atmospheric chemistry leading to formation of particulate nitrate is quite complex. The rates of transformations depend on the concentrations of many intermediate species (including ammonia and free radicals) involved in reactive organic gases and NO_X photochemical system. Ambient concentrations of secondary particles (e.g., secondary organic aerosols, SOA) are not necessarily proportional to the quantities of their precursor emissions since the rates at which they form and their gas/particle equilibria may be controlled by factors other than the concentration of the precursor gas. The rate of NO_X oxidation and the branching ratio between inorganic and organic nitrates depend on the specific environmental conditions in addition to reactant concentrations (Seinfeld and Pandis, 1998).

Fine particles typically are comprised of sulfate, nitrate, ammonium, elemental carbon, organic compounds, and a variety of other compounds. Limited studies (Stoeckenius, et al., 1998a) indicate that there may be changes in the secondary components due to increased oxidants during weekends. Thus, given the contribution of NO_X and VOC to secondary PM formation, it would be useful to know whether the variations by day of week in these precursors are evident in PM data.

The assessment of day-of-week differences in particulate matter concentrations is challenging for several reasons. First, much of the historical PM data consists of 24-hour air samples collected on filters once every 6th day, with PM_{10} mass determinations only. Second, variations of PM-generating processes (e.g., wood-burning in fireplaces, forest fires) on longer time scales may introduce seasonal variability that greatly exceeds day-of-week variations. Finally, the PM constituents of most interest here are $PM_{2.5}$ nitrate, and all particles in the 0.1-1 μm size range, whereas most of the PM measurements do not provide the appropriate size or chemical resolution.

3.1.3 PM Related Data Resources

The particulate data used in this study were available from the U.S. EPA's Aerometric Information and Retrieval System (AIRS) through which data are reported from California's routine particulate matter monitoring programs (i.e., PM10-SSI, Dichot, and TEOM samplers operated by the ARB and local air pollution control districts). Data from the California Acid Deposition Monitoring Program (CADMP) were also used. With the routine monitoring program, samples of particulate matter 10 microns or less in diameter (PM10) are collected over a 24-hour period using a high volume sampler equipped with a size selective inlet (PM10-SSI) or using a dichotomous (Dichot) sampler. Samples are usually collected from midnight to midnight every sixth day. Compositional analysis currently provides measurements of nitrate, sulfate, ammonium, chloride, and potassium for selected sites. The dichotomous sampler, or virtual impactor, uses a low volume PM10 inlet followed by a split in the flow stream that separates particles into two separate fractions: fine particles (PM2.5, i.e., particles with diameters less than 2.5 μm) and coarse particles (those having diameters 2.5-10 μm). The sum of the fine and coarse fractions provides a measure of total PM10 from the Dichot sampler.

The CADMP sampler (Watson, et al., 1991) has two sampling units designed for collection of particulate species in two size fractions and for collection of acidic gases. The PM10 unit collected particles less than 10 μm aerodynamic diameter on a Teflon filter, and had impregnated back filters for collection of ammonia and sulfur dioxide. The Teflon filter was analyzed for sulfate, nitrate, chloride, ammonium, sodium, magnesium, calcium, and potassium ions. The PM2.5 unit collects two samples of particles less than 2.5 μm aerodynamic diameter, one on a Teflon-nylon filter pack without a nitric acid denuder, and the other on a nylon filter after a denuder (consisting of anodized aluminum tubes). The Teflon filter is analyzed for the same species as the PM10 Teflon filter while the nylon back filter is analyzed for nitrate ions. Concentrations of dry-deposition particles were measured by collecting consecutive 12-hour daytime and nighttime samples (day: 0600 to 1800 PST; night: 1800 to 0600 PST), once every sixth day.

Over the years, as the data were reviewed and the relatively limited extent of the acid deposition problem in California became known, the number of pollutants sampled and the number of sites declined. In September 1995, the CADMP network was reduced to five monitoring sites primarily in urban areas (i.e., Azusa, Bakersfield, Long Beach, Los Angeles, and Sacramento). The sample collection was changed from two 12-hour samples to one 24-hour sample commencing at midnight to match the schedule in the PM monitoring network; the sampling program was reduced to PM2.5 only.

The CADMP sampler data, collected after September 1995, have been used for identifying trends in fine particulate mass and its species and evaluating the U.S. EPA sampling method in urban areas. The results of cross-checking the CADMP data against the Federal Reference Method (FRM) data has been used to identify the suitability of the U.S. EPA sampler in urban areas for the desired applications, and to ensure continuity between past and future PM2.5 data in California. As the similarities between the CADMP and the recently promulgated national program for fine particulate matter become apparent, there was no need to continue the CADMP effort. Consequently, ARB terminated the CADMP monitoring program in May 2000.

The PM10 Technical Enhancement Program (PTEP) monitoring (Kim, et al., Part 1, 2000 and Part 2, 2000) was established at six sites including: downtown Los Angeles, Anaheim, Diamond Bar, Rubidoux, Fontana, and San Nicolas Island. At each location, the sampling equipment was deployed to collect fine and coarse particulate fractions for speciation as well as gas-phase nitric acid, elemental carbon, ammonium, and metals. Total mass, collected on Teflon filters, was determined gravimetrically and the concentrations of 36 trace elements were determined by energy dispersive x-ray fluorescence. Quartz fiber filters were used to collect samples to be analyzed for organic carbon and elemental carbon using an optical thermal carbon analyzer. Water-soluble ionic species, such as nitrate, sulfate, ammonium, chloride, and sodium were extracted from the quartz filters and analyzed by ion chromatography.

Two gaseous species, nitric acid and ammonia, were determined by the denuder difference method. Denuders are based on differences in the diffusion properties of gases compared to particles. The difference between the total nitrate measured by the filter pack and that by the nylon filter below the denuder is a measure of gaseous nitric acid by the "denuder difference" approach. PTEP sampling was conducted on a once every sixth day schedule (except for Rubidoux, which was sampled once every third day) from January to March of 1995. The sampling frequency was increased to once every third day from April to June, and then to every day from July to December 1995 (except for San Nicolas Island which remained on a one-in-six day schedule for the entire year). During the second half of 1995, although sampling was scheduled every day (except at San Nicolas Island), PM10 and PM2.5 chemical speciation were conducted only every third day. However, PM10 and PM2.5 masses were determined for each daily sample. During the PM episodes (October 17-20 and November 14-19), chemical speciation was conducted every day (Kim et al., Part 2, 2000).

Continuous particulate monitoring methods have evolved in recent years. Their hourly data provide additional insight into the nature of the particulate problem and remove uncertainties associated with one-in-six or one-in-three day sampling frequencies. The more commonly used continuous PM monitor in California is the tapered element oscillating micro-balance (TEOM). A potential limitation of this monitor is that it is heated to 30 - 50 degrees Celsius to eliminate humidity effects under a broad range of ambient operating conditions. At locations and times for which semi-volatile secondary particles, such as ammonium nitrates and some organics, are a significant portion of the total particulate mass, the PM measurements are lower with the TEOM than with the traditional high-volume sampler with SSI. Another commonly deployed continuous mass instrument is the Beta Attenuation Monitor (BAM). With size selective inlets, these instruments can monitor PM2.5, PM10, or total suspended particulate matter (TSP). Only recently have continuous instruments been designed to permit analysis for ionic and elemental constituents (e.g., carbon, nitrates, and sulfates).

Depending on their size and composition, particles can preferentially scatter or absorb light. Coefficient of haze (COH) and nephelometer (B_{scat}) measurements provide an indication of the relative contributions of light absorption and light scattering. The COH is a direct measure of the light-absorbing ability of the particles. Light absorption is primarily due to elemental carbon from combustion. The nephelometer roughly measures all scattering by fine particles. The characteristics of light scattering are extremely sensitive to the size of the scattering particles. Light scattering by the large particles (>10 μm diameter) is generally not significant. As particle sizes approach the range of light wavelengths (0.1-1 μm) they become dramatically more efficient in light scattering. COH units are defined as the quantity of particulate matter that produces an optical density of 0.01 on the paper tape. A photometer detects the change in the quantity of light transmitted through the spot as the particulate matter collects on the paper filter tape and produces an electrical signal proportional to the optical density. A COH of less than 1.0 represents relatively clean air while a COH of greater than 2.0 represents air with a relatively high concentration of primary combustion-generated particles and secondary aerosols formed in the atmosphere.

From 1989 through 1998, the SSI-PM10 sampling network included 21 sampling sites in the South Coast Air basin (SoCAB). Of these, Avalon and Los Alamitos had very limited data and were not analyzed. SSI-PM10 data were also analyzed for three other air basins: San Francisco Bay Area (11 sites), Sacramento Valley (14 sites), and San Joaquin Valley (14 sites). SSI-PM10 species used in this study include only nitrate and sulfate ions. Although there may be changes in secondary PM components due to increased oxidants during weekends, we focus here on nitrate and sulfate ions because of limited data availability for other species. The sampling record for PM10 has reached a decade in most areas. During the 1990s, PM10 concentrations have declined in almost all air basins and particularly in the SoCAB.

In the SoCAB, three of the 19 PM10-SSI sites also have dichotomous samplers operating in parallel: Azusa, North Long Beach, and Riverside-Rubidoux. To assess the comparability of the SSI-PM10 and Dichot sampling methods, PM10 measurements, matched by site and date, were plotted against each other. Most of the collocated data indicate good agreement between these two sampling methods. The quality of the CADMP data is comparable to that of the other PM2.5 and PM10 samplers and is a valuable source of data that has been largely untapped by data analysts.

3.1.4 Methodology

The basic approach was to analyze ambient PM10 and PM2.5 concentrations for day-of-week patterns. One complicating feature of filter-based sampling is that the samples are generally only collected every 6th, or sometimes every 3rd, day. While this schedule increases the independence between the data points, it also reduces the power of the statistical tests. Statistical tests were performed to provide an indication of the magnitude of the systematic differences between days of the week relative to random day-to-day variation. Where significant differences exist, additional analyses were undertaken to determine which species contribute to the differences.

Since the annual California ambient air quality standard for PM is based on the geometric mean (useful for characterizing lognormal data), the geometric means of SSI-PM10 mass concentrations were calculated for each day of the week for each site for the 10-year period, 1989-1998. The pattern showed Sunday having generally lower PM10 concentrations than other days of the week. However, to determine statistical significance of the differences between days of the week, a rigorous analysis was performed as described below.

The PM10 data were adjusted for seasonality and trend by taking residuals (differences between actual and fitted values) from a smoothing spline. Splines have an advantage over other smoothing methods when applied to complex data sets in that their degree of smoothness is locally adaptive, rather than being uniform over the range of the data. The degree of smoothness was selected by generalized cross validation to yield a curve that followed the seasonal pattern and trend. The residuals (observed value minus fitted value) from the spline fit, henceforth referred to as the *adjusted concentrations*, were largely uncorrelated and symmetrically distributed. To ensure that the seasonal adjustment procedure did not introduce random artifacts, the results based on adjusted concentrations were compared against results based on geometric means of the observed PM concentrations. There were minor discrepancies, but they do not affect the overall conclusions.

Treating the adjusted PM10 concentrations for different days of week as independent, group means and standard errors were computed. The assumption of independence is reasonable because PM samples are collected 6 days apart, long compared to the time scale of daily meteorological events which strongly impact day-to-day PM concentrations.

Day of week PM concentrations were compared for different days of the week by examining error bar charts of adjusted concentrations (see attached charts). The width of the error bars was set to a 97.5% confidence interval to yield an approximate 95% confidence level for pair-wise comparisons between days. If the error bars for two days do not overlap, the means are significantly different at the 95% level of confidence. Numbers next to the means indicate the sample sizes.

The above test of significant differences between days of the week was performed for SSI-PM10 at all 19 sites and various PM species at the three collocated dichotomous and CADMP sites. To confirm the statistical results, the SAS GLM (general linear model) procedure was used to perform analysis of variance on day-of-week means, including fixed effects for month crossed with year. In order to stabilize the error variance and reduce the effect of extreme observations, we transformed the data according to the relationship $y = \log(x)$, rendering the transformed data as normally distributed since the original data are log-normally distributed. We compared the GLM significance levels for pair-wise comparisons of days of week against the error bar charts. The GLM tends to report slightly higher significance levels than the charts, which is expected since the confidence bounds used to generate the charts are conservative.

For the 3 collocated dichotomous, SSI, and CADMP sites, geometric means by day of week of the PM10 and PM2.5 mass and species were calculated. Also, for the 3 dichotomous and CADMP sites, geometric means for separate seasons (winter, spring, summer, and fall) and separate time periods (1989-1991, 1992-1994, and 1996-1998) were calculated. The 3-year data means were selected to avoid the changes due to the introduction of reformulated gasoline regulations in 1995. Federal reformulated gasoline was introduced in Los Angeles beginning in the Spring of 1995, and California cleaner-burning gasoline was introduced statewide in the Spring of 1996. Data for 1995 was excluded because, as a transition year, it was not to be representative of either period.

For the PTEP data, the means are arithmetic means of quarterly arithmetic means, where the quarters are defined to be: Quarter 1 – Jan-Mar; Quarter 2 – April-June; Quarter 3 – July-September, and Quarter 4 – October- December of 1995. Unlike the SSI and Dichot data sets, where the sampling frequency was equal across months, the PTEP data had uneven sample sizes for the months. Hence, this calculation was adopted to better reflect the unequal sample count and to mirror U.S. EPA standard calculations of the means of quarterly arithmetic means.

The crustal component of both PM10 and PM25 was calculated by:

Crustal=2.20*Al + 2.19*Si + 1.63*Ca + 2.42*Fe + 1.94*Ti.

Similar statistical methods were applied to the SSI-PM10, Dichot, and CADMP as applied to the PTEP data (that is, spline smoothing, residuals, then 97.5% confidence bars, etc). The PTEP graphs indicate the confidence intervals for significance testing on the total mass of PM10 and PM2.5. Similar graphs of confidence intervals were also created for the various species of PM10 and PM2.5 (graphs are not presented).

3.1.5 Discussion of Results

3.1.5.1 South Coast Air Basin

The most abundant components of PM10 and PM2.5 in the SoCAB are ammonium, nitrate, sulfate, organic carbon, and elemental carbon (Hughes et al., 1999). Aluminum, silicon, calcium, manganese, and iron are abundant only in coarse PM10. The concentration of crustal components is low in urban areas, where most of the road surfaces are paved. Aerosol nitrate is the largest chemical component of both PM10 (23-26% of the PM10 mass) and PM2.5 (28-40% of the PM2.5 mass) in the Basin.

Aerosol nitrate originates from atmospheric reactions following the emission of NO_X (NO or NO_2) and VOC gases from motor vehicles and other combustion sources. Aerosol organic carbon is directly emitted from numerous source types including motor vehicles, wood smoke, and food cooking. Gas-phase organic compounds also can react in the atmosphere to produce low vapor pressure products that condense to form secondary organic aerosols. The major components of the “others” (unexplained portion of the measured PM mass) in the PTEP database are water and trace metals, and in the CADMP database are organic compounds, water, and trace metals.

Table 3.1-2 displays the average PM10 concentrations by day of the week for 17 sites in the SoCAB from 1989 to 1998. Analyses of PM10 mass from the SSI samplers and three collocated CADMP samplers (at North Long Beach, Azusa, and Downtown LA) show that Sunday is the lowest PM10 day of the week at 15 of 17 locations, often significantly different from mid-week. This might be due to the lower car and truck traffic on Sundays compared to mid-week and the associated decrease in road dust and emissions of PM and PM precursors. The Saturday mean concentration is comparable to weekday concentrations but generally slightly lower than concentrations on Friday. Roughly half of the sites show a slight dip in PM10 concentrations on Wednesday. Some sites show Thursday as having the highest PM10 during the week.

Table 3.1-3 displays annual average SSI PM-10 nitrate concentrations at 15 sites in the SoCAB. The highest annual average particulate nitrate concentrations are usually observed at Rubidoux-Riverside and Fontana. Examination of the 1997-99 results indicates a weekly pattern with the maximum particulate nitrate concentrations occurring on Monday or Wednesday and the minimum occurring on Saturday or Sunday at several sites, including Azusa, Los Angeles North Main, Riverside-Rubidoux and Fontana. At 14 of the 15 locations, the weekend average was lower than the weekday average for PM-nitrate. Across all 15 sites, weekend PM-nitrate concentrations averaged 13% lower compared to the weekday average.

Table 3.1-3 shows two additional patterns. First, average PM-nitrate concentrations in 1997-99 were substantially lower on Sunday, Tuesday, and Saturday for almost all sites compared to 1988-91. These decreases in PM-nitrate coincide with decreases in ambient NO_X concentrations. Second, the PM-nitrate data show changes by day-of-week that are highly variable. For example, at Downtown L. A., Tuesday showed a strong decrease from 1988-91 to 1997-99 while Wednesday showed a strong increase followed by a decrease on Thursday. These day-of-week differences in the trend have no obvious explanation and raise questions about adequacy of the data collected on a 1-in-6-day schedule. Nitrate particle losses in current sampling methods are very high due to volatilization of ammonium nitrate under changing conditions of temperature and relative humidity during sampling and transport of the filter samples. These losses can be as large as 50 percent, resulting in an underestimation of ambient ammonium nitrate particles.

Dichot-PM10 (the sum of coarse and fine fractions) tracks the same pattern as SSI-PM10 at Azusa, North Long Beach, and Riverside. The coarse fraction is significantly lower on Sunday and Saturday at Azusa, but not at North Long Beach and Riverside-Rubidoux. Across the time periods, PM concentrations have decreased considerably. Because the amount of data is limited for each season and period, no significance testing was performed on day-of-week differences, and no results are shown.

Significance testing of CADMP data shows PM10-daytime adjusted concentrations at Azusa being significantly lower on Saturday and Sunday than on weekdays. For the Downtown LA and North Long Beach sites, and for individual species, differences by day-of-week for daytime, nighttime, and 24-hour samples were not statistically significant (95% level).

Analyses of PM10 data from the CADMP and TEOM samplers show that Sunday is the lowest day of the week at three sites in SoCAB, often significantly different from mid-week. Summer PM10 concentrations from a TEOM sampler at Azusa (Figure 3.1-20) averaged 23% lower on Sundays and 19% lower on Saturdays compared to on weekdays, which averaged approximately 62 $\mu g/m^3$.

TEOM-PM10 data do not exhibit the same pattern as the CADMP-PM10 data at Azusa, Downtown LA, and North Long Beach. Weekday TEOM-PM10 changes are less pronounced than those using the CADMP-PM10 data. Across periods, day-of-week patterns of TEOM-PM10 are relatively similar for each season and period.

A systematically low TEOM response in comparison to the integrated gravimetric methods was observed. In a comprehensive study, Allen et al., (1997) reported results in which TEOM data collected at 10 urban sites in the U.S and Mexico were compared with 24-hour integrated mass concentrations for both PM10 and PM2.5. They collected a large data set that included both winter and summer seasons. Allen et al., (1997) concluded that, especially for urban areas, a significant portion of PM10 could be semi-volatile and could be lost from the heated filter in the TEOM, thus leading to a systematic difference between the TEOM and integrated method.

Day-of-week patterns of the TEOM-PM10 data do not track the same pattern as light scattering data at all sites. The day-of-week patterns for light scattering show no change or a small change. Results of a visibility modeling study (Wexler et al., 1992) indicate that light-scattering particles dominate the visibility problem, and light absorption (mainly by black carbon particles) makes an increasingly important contribution to the extinction coefficient in the fall and winter months. Also, the results of this study show that collocated nephelometers are often in disagreement, and that no visibility model can be expected to produce exact agreement with all measured light scattering values because the light scattering data do not agree among themselves. Note that during the 1987 Southern California Air Quality Study (SCAQS), the light scattering values were measured by several investigators using heated or non-heated nephelometers and even slightly different instrumentation for measuring light scattering.

Examination of PM10 mass at each of the PTEP sites indicates a weekly pattern with the maximum concentrations occurring on Thursday or Friday and the minimum occurring on Saturday or Sunday at all five sites. PM2.5 concentrations on Wednesday are lower than on the other weekdays at Anaheim and Rubidoux; however, a PM2.5 Wednesday maximum occurs at Los Angeles-North Main and Fontana. Average PM10 and PM2.5 concentrations showed strong spatial variations with low concentrations in coastal areas and high concentrations in inland areas.

Analysis of the PM species indicates that ammonium and nitrate show a strong spatial variation with low concentrations at coastal locations and high concentrations at inland locations. This is partly due to transported precursor emissions of gaseous ammonia having more time to react with nitric acid. Generally, NO and NO_2 concentrations are much higher than either gas-phase nitric acid concentrations or aerosol nitrate concentrations. Thus, the precursor gases needed for more gas-phase nitric acid production are available in abundance. Excess ammonia is present at most times (high ammonia emissions in the air basin originate near Chino from agricultural and livestock husbandry operations); thus any gas-phase nitric acid formed usually will be driven quickly into the aerosol phase. Sulfate concentrations do not show strong spatial variations. Although elemental carbon concentrations do not show a strong spatial variation, the Los Angeles-North Main site has the highest elemental carbon concentration because it is in the most dense traffic area in SoCAB.

3.1.5.2 Other Regions

The results of the SSI-PM10 data from the San Francisco Bay Area, San Joaquin Valley, and Sacramento Valley show no “weekend effect” for PM10. Though Sunday shows the lowest PM10 concentrations, followed by Wednesday, and then Saturday at many sites, the differences are not statistically significant (95% level). Since there was no significant PM10 effect, we did not investigate PM at the individual species level.

At the Sacramento site, the day-of-week pattern of the TEOM-PM10 data is associated closely with the COH data. Recall that the COH is a direct measure of the light absorbing ability of the particles. Light absorption is primarily due to elemental carbon from combustion.

Since elemental carbon accounts for about 10-15% of total fine particle mass in the Los Angeles Air Basin (Rogge et al., 1993), and up to 30-40% at Moss Landing, (Moss Landing Air Monitoring Program Advisory Committee, 1996), reduced emissions of this primary PM component can potentially contribute to reduced ambient PM concentrations and the associated reduction in light extinction. Traffic count data in the San Francisco Bay Area show a decrease in heavy-duty vehicle travel on weekends (Dreher and Harley, 1998). Since heavy-duty trucks typically represent a major source of black carbon, the decrease in heavy-duty truck travel may also result in a decrease in ambient elemental carbon concentrations, and perhaps a decrease in PM light extinction as well. High concentrations of PM, elemental carbon in particular, may reduce the amount of ultraviolet radiation available to drive ozone photochemistry near the earth’s surface.

3.1.6 Summary and Conclusion

Particulate matter in the air we breathe is a significant health concern. Exposure to particulate pollution is linked to increased frequency and severity of asthma attacks and bronchitis, and even premature death in people with existing cardiac or respiratory disease. Those most sensitive to particulate pollution include people with existing respiratory and cardiac problems, children, and the elderly. All inhalable particles are harmful – both “coarse” particles over 2.5 microns to 10 microns in aerodynamic diameter and “fine” particles, those 2.5 microns or smaller.

Fine particles typically are comprised of sulfate, nitrate, ammonium, elemental carbon, organic compounds, and a variety of other compounds. Secondary ammonium nitrate is generally the largest contributor during the winter at most of the urban sites in California. The results of several studies indicates that during some episodes of high particle concentrations in California, ammonium nitrate – formed secondarily from NO_X and ammonia emissions – can account for over half of the PM2.5 mass. One factor contributing to increased PM2.5 concentrations in the winter is meteorology (cool temperatures, low wind speeds, low inversion layers, and more humid conditions) that favors the formation of secondary nitrate and sulfate.

The formation of secondary particles, which are a major contributor to the fine PM levels in California, from gas-phase precursors is a complex, nonlinear process. Consequently, a one-to-one relationship between precursor emissions and ambient secondary PM concentrations is not expected. The rate of NO_X oxidation and the branching ratio between inorganic and organic nitrates are known to depend on the specific environmental conditions in addition to reactant concentrations. The partitioning of inorganic nitrate between gaseous nitric acid, ammonium nitrate, and nonvolatile nitrate is known to depend on a number of factors, such as relative humidity, temperature, and ammonia, in a nonlinear manner. Understanding how particulate ammonium nitrate is formed and how to effectively reduce it through controls on NO_X and/or ammonia sources is a critical part of California’s PM2.5 program.

Analyses of PM concentrations for all, or part of, 10 years (1989 – 1998) showed the following:

- PM concentrations have declined.
- SSI samplers reported the lowest average PM10 concentrations on Sundays at 15 of 17 locations in the SoCAB; however, the pattern is not statistically significant at all sites.
- Dichotomous samplers reported the lowest average PM2.5 on Sundays at all three locations in the SoCAB.

- Summer PM10 concentrations from a TEOM sampler at Azusa averaged 23% lower on Sundays and 19% lower on Saturdays compared to the weekdays, which averaged approximately 62 $\mu g/m^3$.

- In the San Francisco Bay Area, PM10 from SSI samplers was lowest on Sunday, followed by Wednesday, and then Saturday. However, these differences did not achieve statistical "significance".

In general, some day-of-week comparisons for particulate matter concentrations are difficult to interpret. No simple explanation for this phenomenon in terms of source strengths, atmospheric chemistry, or meteorology is readily available. However, it should be mentioned that nitrate particle losses in current sampling methods are very high due to volatilization of ammonium nitrate under changing conditions of temperature and relative humidity during sampling and transport of the filter samples. After sample collection in the field sampler, a delay before the filter packs are picked up could allow significant volatilization of particulate nitrate. These losses can be as large as 50 percent, resulting in an underestimation of ambient ammonium nitrate.

Ambient concentrations of secondary particles are not necessarily proportional to the quantities of emissions since the rates at which they form and their gas/particle equilibria may be controlled by factors other than the concentration of the precursor gas. For example, several factors influence the relationship between NO_X emissions and particulate nitrate concentrations, which might act to reduce the impact of decreases in weekend NO_X emissions on ambient 24-hour average nitrate concentrations. The photochemical conditions that lead to higher ozone on weekends may also increase the fraction of NO_X that is converted to nitric acid and particulate nitrate. Also, PM measurements summarized in several studies are from 24-hour integrated samples and thus represent the influence of emissions throughout the day. While morning NO_X emissions are reduced on weekends, emissions at other times of the day might not differ significantly between weekends and weekdays. Despite the complex non-linear relationship of PM-nitrates to NO_X emissions, it appears that PM-NO_3^- is much less responsive to VOC controls when ozone formation is VOC-limited than it is to NO_X controls qhen the ozone photochemistry is NO_X-limited (Harley et al., 1997).

In summary, analysis of particulate matter concentrations indicates a general weekly pattern with the maximum occurring late in the workweek and the minimum occurring on weekends (especially Sunday); however, the pattern is not statistically significant at all sites and areas. Given the wide variety of sources contributing to PM and the factors listed above, interpretation of these results in terms of weekday/weekend emissions differences is complex and should be done with caution. Most likely, the standard (once-every-sixth-day) monitoring measurements from the regulatory network would not be sufficient. Daily (24-hr means) and continuous monitoring of PM10 and PM2.5 masses and species (nitrate, sulfate, organic carbon, and elemental carbon) would provide information that would be more useful in relating atmospheric measures to the proposed hypotheses.

Several field studies have already provided further data for understanding the weekend effect. A comprehensive analysis of data from the PETP2000 in southern California and the Central California Regional Particulate Air Quality Study (CRPAQS) should be pursued. Performing a comprehensive air quality data analysis and three-dimensional modeling study that would test the impact of emissions changes associated with changes in emission levels, timing, spatial distributions, etc, might lead to a more accurate characterization of the weekday/weekend behavior of PM.

However, confidence in the accuracy of air quality models that can count for the size and composition distribution of airborne particles can only be built through extensive testing and evaluation of model performance against ambient data. A recent review of the current status of air quality models that are suitable to simulate PM indicates that particular emphasis should be given to improvement in the model formulation (e.g., secondary aerosol formation, aqueous-phase chemistry, etc.) and development of comprehensive data bases suited for model performance evaluation.

3.1.7 Recommendations

Existing studies indicate that aerosol ammonium nitrate formation in California is typically not limited by the availability of ammonia. However, existing work from the San Joaquin Valley Integrated Monitoring Study of 1995 (IMS95) suggest that VOC reductions may reduce the rate of aerosol formation more effectively than NO_X reductions in areas where ozone formation is VOC-limited. Additional research efforts should be directed to this topic. It is desirable to conduct an extensive gas-phase measurement program to characterize speciated VOC, NO, NO_2, O_3, H_2O_2, HNO_3, and if feasible, OH, NO_3, HO_2, and RO_2 during winter. Other oxidized nitrogen species, including HNO_3, particulate nitrate, HNO_2, PAN, and organic nitrate, should be measured to improve the understanding of nitrogen chemistry. This database would also be suitable for testing current mechanisms, such as SAPRC and CBM-IV which have not been thoroughly tested under wintertime conditions that are conductive to PM formation.

Photolysis rates are reduced within the fog layer but increased above it due to back scattering of sunlight. In light of the effects of the photolysis reactions on the chemistry of NO_3 and N_2O_5, measurements of the solar flux (UV and broad radiation) are recommended.

Aerosol measurements by a specially equipped aircraft during the 1997 Southern California Ozone Study (SCOS97) revealed multiple aerosol layers with a complex vertical structure. The overall picture obtained from these airborne observations is a highly complex aerosol structure that is not consistent with a simple representation of a mixed layer between the ground and a temperature inversion. Additional measurements are necessary to determine whether the presence of these strong gradients follows a diurnal pattern.

The impact of meteorological variables on PM mass and its components also needs to be evaluated further. Weather plays a big role in what primary particles are emitted, and to what degree. Secondary pollutant formation is influenced by a combination of precursor pollutant concentrations and weather conditions. Conversion of SO_X to sulfate aerosols is accelerated by the presence of oxidants and OH radicals in the air (as during ozone episodes) and is accelerated even more under humid conditions when the conversion can occur inside water droplets. NO_X conversion to particulate nitrate is even more sensitive, as formation rates must compete with dissociation back to gases, so that particulate nitrate is generally a cool-wet (e.g., winter) phenomenon.

Until recently it was assumed that the end product of the tropospheric NO_X was nitric acid. However, a recent research project conducted under ARB sponsorship (Mochida and Finlayson-Pitts, 2000) has shown that nitric acid on a surface can react with NO to regenerate NO_2 which can then form particulate nitrate. Preliminary modeling studies suggest that this reaction may increase the formation of particulate nitrate and that existing models underestimate the benefit of NOx controls for reducing PM and ozone. An additional research contract is continuing with a focus on providing a more complete understanding of the effect of heterogeneous nitrogen chemistry on ozone and particle formation. The information gained in this project may have very serious implications as to effectiveness of control strategies for both ozone and PM.

Further research is recommended on developing additional measurement methods that provide high-time resolution data on PM nitrate, carbon particles, and light scattering and absorption by aerosols. Concurrently, additional research is needed to understanding the temporal (and spatial) variations in PM-generating processes. To thoroughly evaluate the aerosol and UV radiation hypothesis, it will also be necessary to measure the particles in the 0.1 – 1 micron size range (not a standard size measurement at this time) and to make more measurements of sunlight in the UV spectrum.

3.1.8 References

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Table 3.1-1. Calculated exceedances of ambient standards for particulate matter in selected air basins during two periods in California

Standard and Region	Average Exceedances* from 1988 to 1990	Average Exceedances* from 1997 to 1999
National 24-hour PM10 Standard		
South Coast Air Basin	27	4
San Joaquin Valley Air Basin	31	10
California 24-hour PM10 Standard		
Sacramento Valley Air Basin	99	50
San Francisco Bay Area Air Basin	78	24

*The number of exceedances is "calculated" as if sampling was done daily.

Table 3.1-2. Average annual PM10 concentrations at locations in the South Coast Air Basin based on measured data from SSI samplers in 1989 through 1998

			Average PM10 by Day-of-Week (ug/m3)						
Site	**County**	**Obs.**	**Sun**	**Mon**	**Tue**	**Wed**	**Thu**	**Fri**	**Sat**
Hawthorne	Los Angeles	25	29.0	31.5	34.6	31.8	40.0	36.3	31.9
North Long Beach	Los Angeles	21	30.2	34.7	38.9	35.6	38.8	38.0	35.0
Azusa	Los Angeles	25	36.0	43.2	46.5	40.6	52.5	49.6	39.0
Burbank-W Palm Avenue	Los Angeles	25	34.0	39.9	41.1	40.2	44.3	48.3	37.7
Santa Clarita-County Fire Station	Los Angeles	25	28.7	30.3	33.0	29.8	35.4	36.6	30.4
Los Angeles-North Main Street	Los Angeles	25	34.5	37.3	39.4	41.7	45.2	45.2	39.0
El Toro	Orange	26	28.2	32.0	31.1	29.1	34.5	37.1	29.6
Anaheim-Harbor Blvd	Orange	25	30.7	38.1	38.0	36.8	39.8	41.9	31.2
Norco-Norconian	Riverside	23	42.0	44.4	47.3	45.9	53.0	52.9	41.5
Banning-Allesandro	Riverside	25	24.2	38.1	37.7	32.6	37.0	38.5	27.0
Perris	Riverside	26	34.0	37.9	46.2	38.9	50.4	45.3	34.5
Riverside-Rubidoux	Riverside	27	50.7	62.8	63.5	54.8	64.3	67.0	58.8
Redlands-Dearborn	San Bernardino	23	35.8	38.2	45.9	44.2	50.2	45.6	42.4
San Bernardino-4th Street	San Bernardino	25	42.3	45.9	52.8	46.3	58.8	56.7	46.3
Fontana-Arrow Highway	San Bernardino	25	40.8	53.9	56.8	51.0	62.0	60.9	46.1
Ontario-Airport	San Bernardino	25	41.8	47.1	52.8	45.5	57.3	54.7	49.0
Crestline	San Bernardino	26	21.8	23.1	25.6	21.4	24.1	26.2	27.1

Table 3.1-3. Average annual PM10-nitrate concentrations at locations in the South Coast Air Basin based on measured data from SSI samplers

		Day of Week Average Concentration						
Location	**Years**	**Sun**	**Mon**	**Tue**	**Wed**	**Thu**	**Fri**	**Sat**
Hawthorne	**1988 to 1991**	3.5	4.7	4.9	4.9	5.3	3.4	4.9
	1997 to 1999	4.5	4.6	4.9	5.0	5.1	4.5	4.2
	change	29%	-2%	-1%	2%	-5%	35%	-15%
San Bernardino-4th Street	**1988 to 1991**	11.5	13.7	10.0	9.6	7.7	12.0	9.3
	1997 to 1999	8.3	9.8	7.9	7.8	8.8	8.4	7.3
	change	-28%	-28%	-21%	-18%	15%	-30%	-21%
Fontana-Arrow Highway	**1988 to 1991**	9.5	13.1	9.8	9.3	7.4	10.8	8.6
	1997 to 1999	6.7	8.9	7.0	9.4	6.9	8.3	6.5
	change	-29%	-32%	-29%	1%	-7%	-24%	-24%
Ontario-Airport	**1988 to 1991**	10.0	13.4	11.0	9.5	8.5	11.7	10.0
	1997 to 1999	6.8	9.2	7.3	8.2	7.4	8.5	6.5
	change	-32%	-31%	-33%	-13%	-13%	-27%	-35%
North Long Beach	**1988 to 1991**	5.1	5.6	5.7	5.2	4.7	3.9	3.8
	1997 to 1999	4.8	5.0	5.4	5.4	5.0	4.3	4.7
	change	-5%	-10%	-5%	3%	6%	8%	23%
Azusa	**1988 to 1991**	6.5	6.9	7.2	5.9	6.0	6.7	6.0
	1997 to 1999	5.3	7.0	4.9	6.7	5.7	6.5	5.4
	change	-19%	2%	-31%	13%	-4%	-3%	-10%
Burbank-W Palm Avenue	**1988 to 1991**	6.6	7.0	7.6	5.9	7.2	6.8	6.6
	1997 to 1999	4.8	6.8	5.3	6.3	5.3	7.0	5.6
	change	-26%	-2%	-30%	7%	-26%	4%	-15%

Table 3.1-3 (Continued)

Location	Years	Day of Week Average Concentration						
		Sun	Mon	Tue	Wed	Thu	Fri	Sat
Lake Gregory	**1988 to 1991**	4.6	4.7	2.9	2.8	4.5	4.7	3.9
	1997 to 1999	2.4	2.3	2.8	2.5	2.5	2.5	2.7
	change	-47%	-51%	-4%	-11%	-43%	-47%	-30%
Banning-Allesandro	**1988 to 1991**	5.8	6.4	5.3	5.0	4.2	8.0	4.4
	1997 to 1999	3.8	5.2	3.7	6.9	4.7	5.2	3.7
	change	-34%	-19%	-30%	38%	13%	-36%	-16%
Perris	**1988 to 1991**	7.1	8.4	6.7	7.6	4.8	8.4	5.6
	1997 to 1999	4.1	6.8	4.9	6.6	5.4	6.0	4.0
	change	-42%	-18%	-27%	-13%	13%	-29%	-30%
Riverside-Rubidoux	**1988 to 1991**	15.9	17.4	16.0	14.9	12.8	15.9	14.8
	1997 to 1999	9.0	13.8	10.1	11.1	11.6	10.0	9.2
	change	-43%	-21%	-37%	-25%	-9%	-37%	-38%
El Toro	**1988 to 1991**	3.9	3.8	4.5	3.9	3.2	3.0	4.5
	1997 to 1999	3.3	4.7	4.5	3.5	3.7	4.0	3.7
	change	-14%	24%	-1%	-10%	14%	32%	-16%
Anaheim-Harbor Blvd	**1988 to 1991**	4.8	5.2	7.3	5.6	6.2	3.8	8.1
	1997 to 1999	4.1	5.3	5.3	4.9	4.6	5.4	4.8
	change	-16%	1%	-27%	-13%	-26%	44%	-41%
Santa Clarita-County Fire Station	**1988 to 1991**	2.9	3.2	3.2	3.3	3.6	2.9	4.2
	1997 to 1999	3.0	3.2	2.6	2.6	2.1	4.0	2.6
	change	6%	0%	-20%	-19%	-43%	39%	-39%
Los Angeles-North Main Street	**1988 to 1991**	5.6	6.4	7.4	5.6	6.4	7.5	6.7
	1997 to 1999	5.1	6.1	5.2	7.5	5.7	6.2	6.1
	change	-8%	-6%	-30%	33%	-11%	-17%	-9%
	Average change	-19%	-13%	-20%	1%	-7%	-7%	-18%